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A STUDY OF THE SOLID AND LIQUID PHASES OF MILK FAT

by

JULIJANA VASIC

A THESIS
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

A STUDY OF THE SOLID AND LIQUID PHASES OF MILK FAT

submitted by Julijana Vasic in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

The ratio of solid to liquid phases determines certain rheological characteristics of milk fat. For this reason some of the factors that influence this ratio were estimated. One of the factors influencing the solid to liquid ratio is the thermal treatment of the fat. By using suitable thermal treatments it is possible to change the physical properties of butter to a certain extent.

Pure winter and summer milk fats were examined, and several thermal treatments were used: rapid cooling to 0°C, rapid cooling with subsequent tempering at 15° and 25°C respectively and stepwise cooling with the first step at 15° and 25°C respectively. The analyses were carried out by means of dilatometers of the volumetric type.

The highest solid fat content was obtained in rapidly cooled milk fat whereas tempering and stepwise cooling promoted decreased solid fat content as a result of formation of different types of crystals. Thermal treatments had no influence on the coefficients of thermal expansion of solid and liquid milk fat. The coefficients of thermal expansion of solid and liquid milk fats differed from each other.

The thermal treatments used did not influence the melting dilation of milk fat, but the melting dilations of winter and summer milk fats were found to be different. The rates of melting were greatly influenced by the thermal treatments. Rapidly cooled milk fat had the highest and fat tempered at 25°C the lowest rate of melting.

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A STUDY OF THE SOLID AND LIQUID PHASES OF MILK FAT

INTRODUCTION

The solid fat content is one of the major factors in determining some of the physical properties of plastic fats. In milk fat, with its complex composition of fatty acids and glyceride structure, there are many variables which may influence the solid fat content. Milk fat crystals may vary in size, as well as in composition. The measurement of the quantity of solid fat in a product is not a simple task and can be done by a number of procedures, many of which involve elaborate and expensive equipment. For purposes of quality control, a simple procedure is desirable and the dilatometric method is the most widely used.

It has been known for a long time that the crystallization behaviour of milk fat can be influenced by modification of the thermal treatments that are used in commercial processes. Many studies have been carried out aimed at finding processing techniques for butter that would result in more desirable textural characteristics. Although some of these procedures have proven successful, their application has been hindered by a lack of fundamental information on the nature of the differences that resulted from these treatments. It is likely that

variations in physical properties of milk fat may result from a combination of several factors, viz., crystal size, recrystallization, mixed crystal formation, and others. Only a systematic study of these changes, preferably carried out on pure fat, would supply the information necessary to understand and explain changes occurring in commercial processing after modification of certain variables.

The objective of the study reported in this thesis has been to collect information on this subject.

REVIEW OF LITERATURE

Crystalline State

Crystals are solids with atoms or molecules arranged in space with particular regularities. Crystals have special spatial arrangement called "habit", in which symmetry is one of the main characteristics. In addition, there are also crystalline solids that have no regular geometric shape because the crystal habit appears in a rather limited space, usually not greatly exceeding the magnitude of the molecular dimensions. Such material is often called polycrystalline, and can be considered to consist of microcrystals which are distributed at random and usually embedded in a matrix of amorphous material. Having different physical properties and behaviour under certain external conditions, these polycrystals can be distinguished from amorphous materials (45).

The structural elements of crystals are atoms, ions, or molecules. The classification of crystals, and the nature of bonds among crystal elements, is made on the basis of the crystal components. Crystal lattices and crystal bonds can be classified (49) as: atomic, ionic, metallic, and molecular, with covalent or ionic bonds.

The units of crystal structure in organic compounds are molecules. The binding forces can be:

Dipole attraction, in molecules that are electrically unsymmetrical, i.e., polar. The polarity is determined by the level of the

charges and the distance between them which is measured by the dipole moment. This can be measured in Debye units, a Debye unit being equivalent to 10^{18} electrostatic units.

Hydrogen bonding is ionic or electrostatic. In fatty acids and other compounds containing the -COOH group, hydrogen bonding is involved. This bonding is relatively strong, especially in fatty acids with lower numbers of carbon atoms, but, of course, hydrogen bonding is not as strong as a true covalent bond.

Van der Waals' forces are electrical in nature and are produced by inductive effects. The polarization of molecules occurs because of electron asymmetry in atoms, which happens during shifting of electrons in atoms.

Molecular crystals have relatively weak attractive forces. This explains some of the physical characteristics of these crystals, for example, they have a relatively low melting point.

Crystallization Kinetics

On cooling of a liquid kinetic energy is lowered, and at the freezing point crystals are formed. At freezing temperature, molecules become oriented in a definite pattern (9) and separate from the liquid (80). Only the slowest and nearest molecules will attach themselves to the crystals; the faster ones are left in the liquid and they will remain in the liquid if cooling does not proceed. Heating has the reverse effect because vibrational energy of the molecules overcomes the binding forces in the crystals; they then begin to melt

and continue to melt if sufficient heat is provided. If no further heat is supplied, the solid and liquid phase remain in equilibrium.

Supercooling occurs when cooling is carried out slowly and without agitation and the liquid reaches a temperature below its crystallization temperature. The liquid is in a metastable state, and by "seeding", or by agitation, crystallization can be initiated. A seed can be of the same substance, or of a substance chemically and crystallographically similar (7).

The crystallization process is determined (35, 68) by:

(i) the velocity of nuclei formation,

(ii) the rate of crystal growth,

(iii) the interrelation between formation and growth.

The velocity of nuclei formation has been expressed (89, 90) as:

$$W = K \frac{P}{L}$$

where,

W = velocity of the process

K = constant

L = solubility

P = total quantity of the disperse phase which will be crystallized when the process is complete

Since the whole of the material of the disperse phase must be present, either as crystals or in solution, then:

$$P + L = Q$$

where,

Q = the total quantity of the disperse phase in a unit volume, i.e., the total concentration.

Then:

$$W = K \frac{Q - L}{L}$$

The second phenomenon depends upon diffusion, and its velocity can be expressed (65) by the equation:

$$dx = \frac{DS}{\delta} (C_2 - C_0)\, dt$$

where,

dx = amount deposited on the surface

D = coefficient of diffusion

S = area of the crystals

δ = thickness of layer through which diffusion is taking place

C_0 = actual concentration of the solution at saturation

C_2 = supersaturation of the solution

dt = time interval.

Only if the thermodynamic potential after precipitation is lower than before can nucleation and growth of crystals occur (58). This means that crystals will be formed only in supersaturated solution.

Generally speaking crystals appear completely developed and in characteristic forms when slow cooling takes place, and when there is free circulation of the liquid around the crystals. Also, under the same conditions, large crystals are formed (56). Crystals, in rapidly-cooled solutions, are not completely developed when a rapid removal of heat causes a fast decrease of kinetic energy of the molecules and increase in the viscosity of the liquid phase (1). Rapid cooling

causes formation of a large number of small crystals. In extreme cases (glass), sudden cooling of complex and long-chain materials causes viscosity increase - even to the extent that further crystallization is impossible (7).

The common fatty acids and glycerides crystallize in similar forms and, therefore, are able to substitute for each other in the crystal lattice. When a fat is cooled slowly, so-called overgrowth, or "layer" crystals are produced. The inner layers of these crystals contain high-melting fatty acids or glycerides, and the lower-melting components occur in the outer layers (1, 87). These layers of crystals have a melting point very close to that of their component glycerides. There is a certain interference of neighbouring layers, and this is the reason that one layer has not exactly the same melting point as its component glycerides. Rapid cooling of melted fat causes formation of "mixed" crystals (5, 8, 19, 21, 23, 26, 28, 57, 63, 86) without distinct layers, which involves a difference in the composition of the crystals. These crystals contain glycerides with melting points that differ one from the other. These dissimilar molecules in the crystal cause an increase in solid fat content (18). The melting point of such crystals is in the range determined by the lowest and the highest melting points of the component glycerides. The fat, containing a mixture of "layer" crystals, will have a wider melting range than the fat containing "mixed" crystals, although both fats contain the same glycerides.

As was pointed out above, crystals can develop only in supersaturated solution, and in the presence of centers of crystallization. In the temperature range where the fat is plastic (from the beginning

to the end of melting), the liquid phase of the fat is always saturated. With fats, there is no distinct difference between solvent and solute, and, with changing of the temperature, some of the solvent can change to the role of solute and vice versa (29).

Plastic Fats

The edible fats can be divided into oils and fats. Oils are liquid at room temperature; fats are solid at room temperature. Fats, such as milk fat, margarine, lard, and shortening, are classified as plastic solids (48, 60).

It is a well known fact that when materials are subjected to a stress there will be a change of the original shape. After removal of the stress, the material will either regain its original shape, or will remain deformed. The extent of deformation depends on the kind of material and the intensity of the stress. The same stress will cause only slight deformations in some, and big deformations in other materials. The property of materials to regain their original shape and volume, after removal of a stress, is called elasticity; materials that remain deformed are called plastic (13, 66, 71, 74, 76).

Materials such as fats, clay, and others are called plastic; metals, rubber, and others, elastic. Plastic materials, under limited stress, show characteristics of solids, and when a stress increases over a certain value, the material starts to flow like a viscous liquid (1). This point is called "yield point". Plastic materials generally have low, and elastic materials high, yield points.

Plastic materials have certain characteristics in common (2):

(i) The material must consist of two phases, solid and liquid.

(ii) The solid phase must be finely dispersed and the particles small enough that the force of gravity on each particle is negligible compared with the interparticle forces. Spatial arrangement of solid particles must prevent flow of the liquid phase.

(iii) The solid-to-liquid ratio should be of a certain magnitude: too low a solid fat content will not greatly influence the flow properties of the liquid phase; too high a solid fat content, on the other hand, will form a strong, interlocked structure and the plastic material will appear as a rigid solid.

A plastic fat is a mixture of liquid and solid phases at room temperature (81). The solid phase is incorporated in such a way as to provide a three-dimensional, self-supporting structure (59). The relationship between the two phases depends chiefly on temperature because lower temperatures result in increased solid content, and higher temperatures, in decreased solid content (1, 47).

The factors that determine the character of plastic fats, including milk fat, are:

(i) Solid fat content

(ii) Size and number of crystals

(iii) Strength of crystal network

(iv) Viscosity of the liquid phase

(v) Heat treatment.

(i) The factor with the most direct influence on physical properties of fats is the ratio of solid to liquid phase. With an increase in solid content, the fat becomes harder and vice versa. For edible fats, a wide plastic range is desirable - this means a mixture of glycerides of widely different melting points, with a small amount of the high-melting constituents.

(ii) Size and number of crystals per unit of weight also influence the physical properties of fats (39, 81). With the same solid fat content, smaller crystals cause greater hardness of fat. Fine crystals give a wider plastic range and a smoother appearance of fats. Crystals composed mostly of high-melting glycerides are more rigid than those containing low-melting glycerides.

(iii) The degree of mutual attraction of crystals, and their tendency to form aggregates, gives strength to the crystal network.

(iv) High viscosity of the liquid phase causes bigger yield stress of the fats.

(v) Heat treatment of a fat has a great effect on consistency at a given temperature (1, 2). Rapidly-cooled fat has a greater hardness (20, 21, 24, 26, 28, 30) but if tempering takes place, the fat will be softer (77). Tempering results in a lower solid fat content and also in a different character of the crystals (64).

The Rheological Properties of Milk Fat

The physical, i.e., rheological properties are of great importance because some of the unique characteristics of fats are physical in nature (59).

There are numerous factors that influence the rheological properties of milk fat. In general, these factors are: chemical composition of the fat, glyceride structure, rate of fat crystallization, ratio of solid to liquid phases, and size of fat crystals (12, 17, 20, 39, 43).

Compared with other animal and vegetable fats, the crystallization behaviour of milk fat appears the most complex (25). Milk fat is a complex system because it contains a large number of fatty acids combined in glycerides. Theoretically, the number of different triclycerides is the third power of the number of different fatty acids. If we were to assume that there are 18 different fatty acids as major constituents of glycerides in milk fat, then 5,832 different triglycerides are possible (82). It is claimed (27, 40, 46, 54) that milk fat triglycerides contain a greater variety of fatty acids than any other natural fat. Seasonal variations must be taken into consideration too, because these variations in chemical composition have a considerable influence on the rheological properties of milk fat (15, 92).

Consistency and plasticity are common names for certain important rheological characteristics of plastic fats. The term consistency is frequently used to express the total of all rheological properties, as apparent viscosity, yield value, etc. Very often, the terms used to

describe rheological properties of plastic fats are confusing because of the lack of standard methods of measurement and, therefore, there are no definite units for the expression of these properties (59).

For the determination of the rheological properties of milk fat, several terms are in use (22, 31):

Hardness. The rheological properties, particularly hardness of butter, are, to a great extent, influenced by the crystal state of the solid phase. The crystal state, on the other hand, depends on the mode of formation of the crystals (24). Hardness is resistance to deformation; sometimes the term firmness is used to describe the same property. Hardness is measured by the penetration method when the deforming body is a cone, a needle, or a cylinder (16, 20, 23, 91); when a taut wire is used, it is designated the sectility method. The measurements are usually carried out in such a way that a deforming body is driven into the butter at constant speed. The force required is then a measure of hardness.

Spreadability. This is a term used for the expression of spreading properties. Special machines have been developed (41, 42, 61, 70) to measure these properties. Spreadability is not a simple characteristic but more or less a mixture of several properties (75).

Setting. This designates the phenomenon of increase in the hardness of butter by keeping it undisturbed after the manufacturing process (14, 16, 42, 62).

Structure. The determining factors of rheological properties are chemical composition and microstructure. Structure is distribution

and arrangement of butter components.

Texture. The term that includes the external manifestation of microstructure is texture. This term is extremely broad (55) and is used to describe several rheological properties such as: moisture distribution, brittleness, oiliness, roughness, smoothness, and graininess (50).

Brittleness. This is related to the ease of fracturing; sometimes butter can crack and break and this will occur in butter with great hardness and coarse crystal structure.

Crumbliness. This expression signifies the relation to an exceptional brittleness combined with a high gas content.

Greasiness. The property caused by low solid fat content and therefore, low hardness; as a consequence there is free oil on the surface of the butter at room temperature.

Review of Methods for Solid Fat Content Determination

The solids content of fats such as butter, margarine, shortening, lard, and others, is of great practical importance because it is one of the determining factors in consistency, which is of interest to both producer and consumer. The measurement of solid fat content, therefore, is an important aspect of the quality control of plastic fats.

There are several methods for the determination of solid fat content which are based on different physical properties of the solid and liquid phases of plastic fats, such as specific heat or thermal capacity,

thermal dilation, dilution of some dyes and electromagnetic properties.

Calorimetry. The method which uses the change of heat content at different temperatures, including latent heat of melting, is the so-called calorimetric method. Determination of heat content is carried out by means of a calorimeter. By measuring the heat content, it is possible to obtain data for plotting heat content-temperature curves.

The calorimetric method for determination of solid fat content is based on the change of heat content with temperature (88). When a material is not homogeneous, but is a mixture of solid and liquid phases, the heat of melting, or solidification, has to be considered.

The specific heat of a substance is the number of calories required to raise the temperature of one gram of the substance by one degree centigrade

$$c = \frac{cal}{g\,^{o}C}$$

Strictly speaking, specific heat is not a constant but depends on the thermal state of the material, or in other words, on the temperature. The law of specific heat change with temperature cannot be derived theoretically, but there are more or less successful empirical equations - one of the most frequently used is:

$$c_t = c_o + \alpha t + \beta t^2 + \gamma t^3 + \delta t^4$$

where,

c_t = specific heat at temperature t

c_o = specific heat at temperature 0^oC

$\alpha, \beta, \gamma, \delta$ = constants

t = temperature at which the specific heat is determined.

A number of factors influence the various members of the equation, such as the kind of material, desirable accuracy of results, and temperature range. We can say that specific heat of the fats is independent of the temperature for temperature intervals where there is only solid, or only liquid phase (1); for instance, for milk fat above 40°C and below -40°C. These approximations are permitted for calculations of solid fat content because absolute values of heat content are not necessary but only their differences.

Dilatometry. The method of determination of solid fat content based on thermal dilation, another well known physical property of materials, is carried out with a dilatometer which could be of a volumetric (3, 34, 36), or gravimetric type (4, 33, 51, 52, 53, 78, 79) and can be static or dynamic (83).

The basic equation showing the dependence of volume on temperature is given by:

$$V = V_o (1 + \alpha t)$$

where,

V = volume at t °C

V_o = volume at 0°C

α = coefficient of thermal expansion

t = temperature.

The coefficient of thermal expansion is assumed constant for the whole temperature range, when the diagram of volume change versus

temperature is used for calculation of the solid fat content.

Dye Dilution. The dye dilution method is one of the modern methods for solid fat content determination. It is based on the property of some dyes being soluble in the liquid phase and insoluble in the solid phase (crystals) of fats (93).

The method is carried out in such a way that a measured quantity of a dye of known concentration is mixed with the fat. After that, separation of the liquid phase can be carried out by ultracentrifugation, filtration under pressure, or capillary absorption. By measuring the absorbance of the liquid phase, it is easy to calculate the amount of liquid phase and, by difference, the solid fat content. The liquid fat content can be computed from the absorbances of the dye solution and the separated liquid fat, in the following way:

$$G_d \times c_d = c_1(G_1 + G_d)$$

$$G_1 = \frac{G_d \times c_d}{c_1} - G_d = \frac{G_d \times c_d \times E}{A_1} - G_d$$

$$G_s\,(\%) = \frac{G_f - G_1}{G_f} \times 100$$

where,

G_f = weight of fat sample

G_1 = weight of liquid phase in sample

G_s = weight of solid phase in sample

G_d = weight of prepared dye solution

c_d = concentration of dye in dye solution

c_1 = concentration of dye in the sample

A_1 = absorbance of sample

E = absorptivity of dye

The Nuclear Magnetic Resonance. This is another modern method of determination of the solid fat content in plastic fats (6, 10). This method uses electromagnetic properties of nuclei, mainly that they can emit or absorb electromagnetic waves under certain conditions, - in the same way as light spectra (emission and absorption) atoms of a substance can absorb (or emit) electromagnetic waves of strictly determined wave length which is determined by the nature of the substance. If a substance is exposed to the activity of electromagnetic waves, of which the frequency is the same as the frequency of the substance, there will be a resonance of vibrations, and atoms of this substance will vibrate in the same rhythm with the external magnetic field. The shape of the resonance line, meanwhile, depends on the physical and chemical properties of the sample, or in other words, on how many atoms are free to orient themselves and enter into resonance (32).

The procedure can be described as follows. First, select one chemical element which exists in the sample and which possesses a nuclear magnetic moment, to serve as an indicator. In the case of fat, this may be C, O, or H, but only the hydrogen atom, or more precisely, the hydrogen nucleus (proton), has an odd mass number and, therefore, may have a nuclear magnetic moment (11). Then, the frequency at which resonance will occur should be determined. The sample is placed in a very strong magnetic field which will cause the orientation of the nuclei. In the solid phase of the sample, molecules are not free to move but they are more or less fixed in their positions in the crystal lattice and, therefore, can vibrate only in a limited manner. Because of the random orientation of the crystals in fats, it can be concluded

that the orientation of our "indicator nuclei" is also random. In the liquid phase of the sample, molecules are free and can be oriented under the influence of the magnetic field, if the external electromagnetic forces exceed the resistance caused by the viscosity (internal interparticle forces).

After the orientation of nuclei under the influence of the strong magnetic field is obtained, a new, relatively weak, variable frequency magnetic field is applied, with the frequency very close to the frequency of the nuclei. The resonant frequency of the nuclei depends, not only on the kind of substance - as was mentioned before, but also on the influence of the neighbouring atoms, the latter being more pronounced in the solid state because of the closer packing of the particles. This means that the energy absorption of the solid state does not occur at a single frequency but is spread over a more or less wide range. At each frequency inside this range, a certain number of nuclei will enter into resonance and, therefore, the energy absorption curve will have a broad, flat shape. On the other hand, due to almost completely uniform orientation of the nuclei in the liquid state, the energy absorption curve will have a sharp, high peak, indicating that almost all nuclei are in the resonance at a single frequency.

By comparing the maximum amplitudes of the energy absorption curves under the conditions of nuclear magnetic resonance of the unknown sample and of the completely melted sample, and multiplying their ratio by 100, the solid fat content, expressed as percentage of the total weight of the sample, can be obtained.

Comparison of Methods for Determination of Solid Fat Content

Each of the methods for solid fat content determination has certain advantages and disadvantages, and the best way to visualize the convenience of one particular method is to review the characteristics of each of the modes of procedure.

The calorimetric method is the oldest and is well established. Many types of calorimeters, for the investigation of plastic fats, have been designed, from simple, classical devices to very complicated, automatically-controlled instruments for maintaining adiabatic conditions during the experiment (69, 73, 84). This method can be static (37, 72), or dynamic (85). Strictly speaking, the impossibility of obtaining a complete temperature equalization of the sample could be a disadvantage because the data obtained by this method would not be absolutely correct. However, this appears to be a theoretical disadvantage only, because by introduction of automatic control and by retaining the experimental conditions, it is possible to maintain the temperature difference within the region of the experimental error. The fact, that before testing it is necessary to prepare the sample by melting and precrystallization (for filling of the calorimeter vessel), makes testing of the original sample impossible.

All the remarks mentioned above about the calorimetric method are applicable to the dilatometric method too because both methods use the thermal properties of fats, viz., heat content and thermal dilation, as an indicator of the solid to liquid ratio. The dilatometric method, on the other hand, appears to be simpler with regard to the equipment

necessary for carrying out the experimental measurements. It can be said, also, that the reproducibility of the results obtained by the dilatometric method is very satisfactory.

The dye dilution and the nuclear magnetic resonance methods do not demand any previous thermal preparations of samples, so that the original state of samples can be examined. On the other hand, one of the most serious disadvantages, in the case of the dye dilution method, lies in the difficulty of separation of the dyed liquid phase from the sample. Several techniques are in use (ultracentrifugation, pressure filtration, capillary absorption in filter paper), but all of them have also certain disadvantages: difficulties in maintaining a constant temperature during ultracentrifugation; capillary absorption separation is too slow.

One of the main disadvantages of the nuclear magnetic resonance method is that it requires very complicated, and therefore very expensive equipment, so, at the present time, only a few laboratories use this technique for investigation of plastic fats.

It appears that one method for determination of solid fat content has no distinct advantage over the others; nevertheless, it can be said that the dilatometric method appears to be superior because of its simplicity and satisfactory reproducibility.

EXPERIMENTAL METHODS

The solid fat content of milk fat was determined by a dilatometric method. The thermal expansion of milk fat was determined in the range from -60° to $60^{\circ}C$. In these measurements, the technique used was a static one, i.e., volume readings were made after complete equilibrium was reached at any one temperature.

Apparatus

The dilatometers used were of the volumetric type. They consist of a glass bulb with a volume of approximately 10 ml (Fig. 1). The filling end of the bulb is stoppered by a ground joint glass stopper, and at the lower end a capillary is attached. The stem is a calibrated capillary tube graduated in mm^3, from 0 to 1,400 mm^3 and, the smallest division of the scale is 5 mm^3. All dilatometers were checked for accuracy, using mercury. Four dilatometers were used, with an overall accuracy as follows:

Dilatometer No. 17	- 0.00190 ml.
Dilatometer No. 21	0.00202 ml.
Dilatometer No. 27	- 0.00160 ml.
Dilatometer No. 28	0.00224 ml.

According to "Official and Tentative Methods of the American Oil Chemists' Society" (67), the accuracy must be at least ± 0.005 ml.

The change in fat volume during the experiment is measured by recording the level of the confining fluid in the stem of the

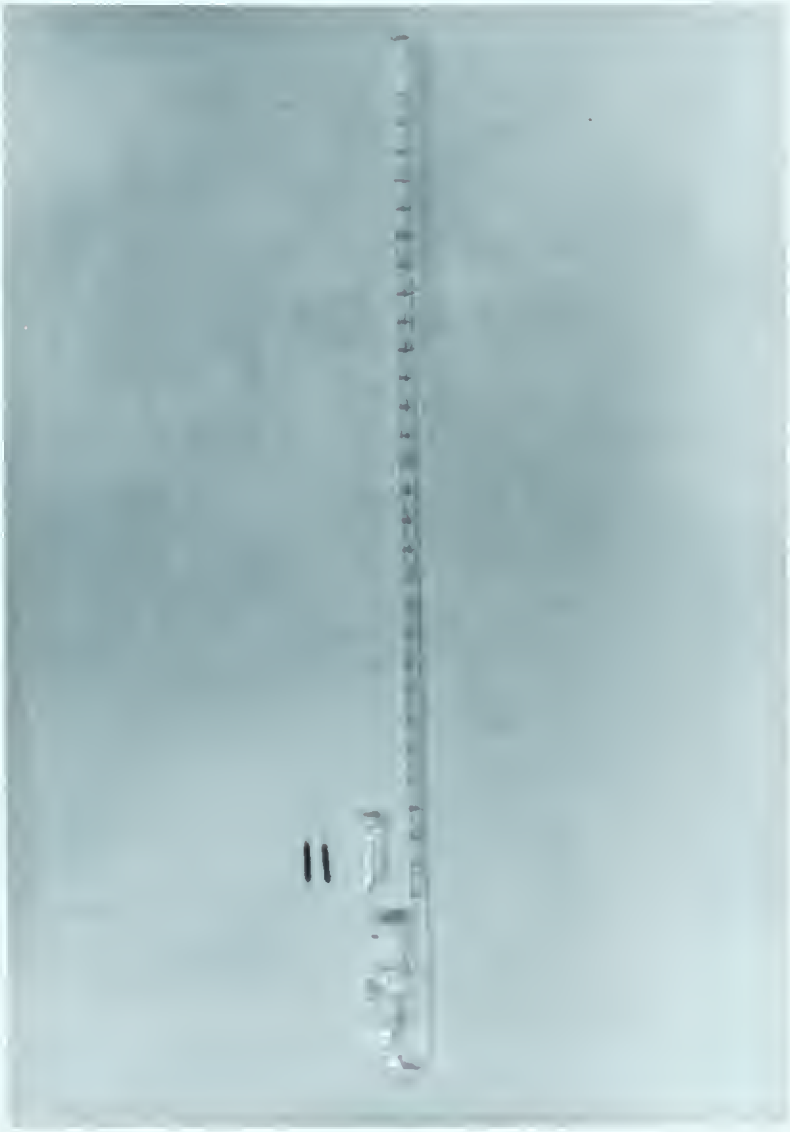

Fig. 1. The dilatometer of volumetric type

dilatometer. A confining fluid, or sealing liquid, is used to prevent entrance of the fat into the capillary tube because, at low temperatures, solidified fat can plug the capillary tube. Confining fluid can be mercury, dyed water, an aqueous salt solution, or an immiscible organic liquid. A confining fluid must have a lower freezing point than the lowest reading temperature used in the experiment. For the investigation of the thermal expansion of milk fat from 10° to 60°C, 1% potassium dichromate was used. It was deaerated by boiling before use. For the temperature range from 5° to -60°C, the confining fluid was a concentrated solution of calcium chloride in 95% ethyl alcohol (freezing point -85°C) (6, 38). When measuring thermal expansion at high temperatures, 2 ml of confining fluid was used; at low temperatures, 3 ml.

For the measurements at temperatures from 10° to 60°C, the dilatometers were placed in a tall, glass cylinder, through which the water from a Hoeppler ultrathermostat was circulated. The measurements from 5° to -60°C were carried out by means of a "Minus Seventy" thermostat bath, with bridge control; the cooling medium was methyl alcohol, cooled by means of dry ice.

Procedure

Pure milk fat was obtained from butter by melting, washing, drying, and filtering. Before filling the dilatometers, the fat was deaerated under vacuum. During deaeration, the flask was agitated regularly to aid in removal of dissolved air.

The dilatometers with confining fluid were weighed before and after filling to obtain the weight of the fat by difference. During filling, special care was taken to avoid inclusion of air bubbles into the dilatometer. Readings were made at 5° intervals. The readings, at each temperature, were taken every 5 minutes until the change in volume was less than 2 mm^3. The total expansion was corrected for the expansion of the confining fluid and of the glass. The thermal expansion of the confining fluid for the high-temperature range (from 10° to 60°C) was taken from the "International Critical Tables" (44). The coefficient of thermal expansion for Pyrex glass, from which the dilatometers were made, is 3.2×10^{-6} mm/mm °C (44). The coefficient of thermal expansion of the confining fluid for the low-temperature range was determined and its value was 0.7115 mm^3/g °C.

Because of the fact that each experiment was done in two parts - one from 10° to 60°C, and the other from 5° to -60°C - two reference temperatures, 60°C and 0°C, were used for calculation of the volume of the fat at different temperatures.

As the first step, the volume of the dilatometer filled up to the zero mark was determined in the following manner. The dilatometer was filled with deaerated, distilled water and the weight of water was measured. The dilatometer was immersed into the water bath and the reading was taken at 60°C. The volume of the dilatometer was then calculated from:

$$V_o\,(60^\circ) = V(60^\circ) - R(60^\circ) = G \times v - R(60^\circ)$$

where,

$V_o(60^o)$ = volume of the dilatometer up to the zero mark at 60^oC, in mm^3

$V(60^o)$ = total volume of water in the dilatometer at 60^oC, in mm^3

G = amount of water in the dilatometer, in g

v = specific volume of water at 60^oC = 1,017.05 mm^3/g. (44)

$R(60^o)$ = reading at 60^oC, in mm^3

For the dilatometers used, the following values were found:

Dilatometer No.	17	21	27	28
$V_o(60^o)$, in mm^3	10,337	11,534	12,024	11,461

For the second reference temperature, i.e., 0^oC, the volume of the dilatometer filled up to the zero mark was found from the equation:

$$V_o(0^o) = V_o(60^o) - \Delta V = V_o(60^o) \times (1 - 60\gamma)$$

where,

$V_o(0^o)$ = volume of the dilatometer to the zero mark at 0^oC, in mm^3

$V_o(60^o)$ = volume of the dilatometer to the zero mark at 60^oC, in mm^3

ΔV = volume contraction in mm^3

γ = coefficient of cubic expansion of Pyrex glass, $\gamma = 3\alpha = 3 \times 3.2 \times 10^{-6} = 9.6 \times 10^{-6}$ mm^3/mm^3 ^oC

The actual volume of the four dilatometers was:

Dilatometer No.	17	21	27	28
V_o (0^o), in mm^3	10,331	11,527	12,017	11,454

In this way, two reference volumes were determined and these values were used in further calculations.

The absolute volume of 10 g of fat at temperature t^o C, was calculated as follows:

$$V_{10\ (t)} = \frac{10}{G} \left(V_{o(rt)} + R_{(t)} - C_d + C_{cf}\right)$$

where,

$V_{10\ (t)}$ = absolute volume of 10 g of fat at temperature t^oC, in mm^3

G = weight of fat in dilatometer, in g

$V_{o(rt)}$ = volume of the dilatometer filled to the zero mark at reference temperature, in mm^3

$R_{(t)}$ = reading at t^oC, in mm^3

C_d = correction for the expansion of the dilatometer between reference temperature and t^oC, in mm^3

C_{cf} = correction for the expansion of the confining fluid, in mm^3

The calculations of V_{10} were made for the temperature range between -60^o to 60^oC at 5^oC intervals and the results were used for the calculation of solid fat content.

Calculation of Solid Fat Content

To obtain a complete series of values, it was necessary to have measurements below the temperature at which milk fat is completely solid and above the temperature at which milk fat is completely liquid.

In other words, it is necessary to obtain the "solid" and "liquid" lines. The "solid" line was obtained by measuring the thermal dilation of milk fat from -40° to -60°C, and the "liquid" line from 40° to 60°C. Both lines were extrapolated in order to cover the whole range in which milk fat is plastic, i.e., in the range where two phases exist. In the Fig. 2, the "liquid" line DE was extrapolated to the temperature of -40°C (section DH), and the "solid" line AB, to the temperature of 40°C (section BK).

The solid fat content (SFC), at temperature t, is now calculated from:

$$\mathrm{SFC} = \frac{\mathrm{GC}}{\mathrm{GF}} \times 100\%$$

Point F represents the imaginary volume of a superheated fat in the solid state, at temperature t^{o}. Point C represents the real volume of fat at temperature t^{o} containing two phases, and G represents the volume of a supercooled fat in the liquid state, at temperature t^{o}. The section GF represents the volume increase during complete melting at constant temperature, since the section GC represents the volume increase caused by melting of the remaining solid phase in an actual case.

Thermal Treatment of Milk Fat

The milk fat used was summer fat, obtained in July, and winter fat, obtained in December; representing soft and hard milk fat. Both fats received a number of different thermal treatments that were carried out after filling the dilatometers with completely-melted milk fat, at approximately 60°C.

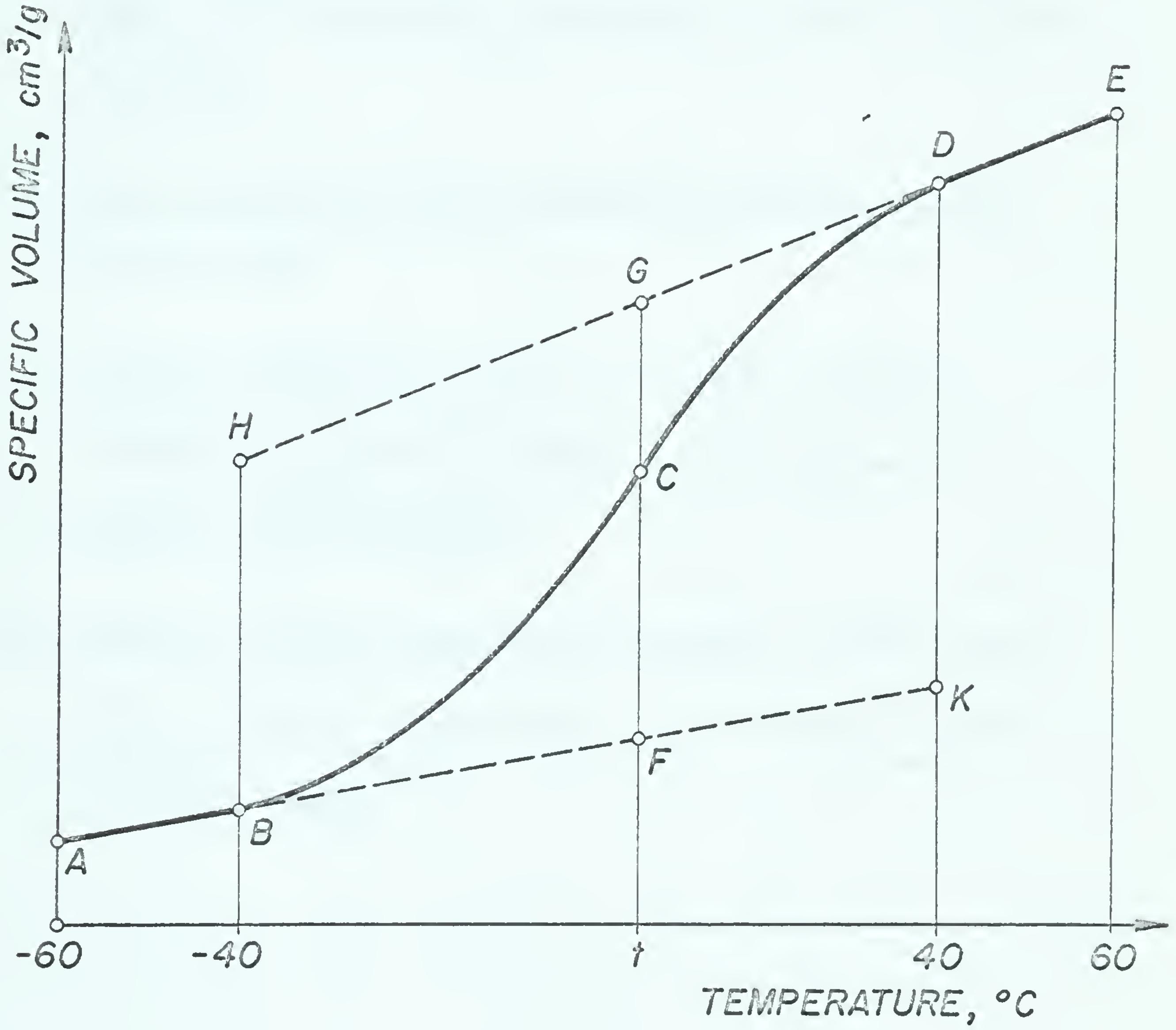

Fig. 2. Schematic drawing of dilatometric curve, showing method of calculating solid fat content

The treatments were as follows:

1. Rapid cooling, by immersion of the dilatometers in an ice-water mixture at 0°C and keeping overnight at 0°C.
2. Rapid cooling, to 0°C, as under (1), and keeping overnight at 0°C followed by tempering in water at 15°C for two hours.
3. Same as under (2) but tempering carried out at 25°C for two hours.
4. Initial cooling by immersion in water at 15°C for two hours, followed by immersion in an ice-water mixture at 0°C overnight.
5. Initial cooling by immersion in water at 25°C for two hours, followed by immersion in an ice-water mixture at 0°C overnight.

RESULTS

The coefficient of thermal expansion

The coefficient of thermal expansion of completely solid milk fat is represented by the slope of the "solid" line and of completely liquid fat by the slope of the "liquid" line, in the volume-temperature coordinate system. For temperature intervals from -40° to -60°C and 40° to 60°C, it was assumed that the coefficients of thermal expansion of solid and liquid milk fat are constants. After the regression lines were calculated from the data obtained by the measurements, it was found that there were only negligible differences between the values obtained from the regression equations and actual volumes of milk fat so that the previous assumption was justified.

For each thermal treatment, four replicates were tested. The coefficients of thermal expansion of solid and liquid fat were found by regression equations for each replicate. The coefficients of thermal expansion of solid fat α_s and liquid fat α_l for winter milk fat are listed in Table 1, and for summer milk fat, in Table 2.

In the text, and in the tables and diagrams, the following notation for different thermal treatments has been used:

Sample series 1, $0^\circ \rightarrow 0^\circ C$	- The melted milk fat rapidly cooled to 0°C and kept overnight at 0°C.

Sample series 2, $0^{\circ} \rightarrow 15^{\circ}\mathrm{C}$	- The melted milk fat rapidly cooled to $0^{\circ}\mathrm{C}$, kept overnight at the same temperature, and then tempered at $15^{\circ}\mathrm{C}$ for two hours before testing.
Sample series 3, $0^{\circ} \rightarrow 25^{\circ}\mathrm{C}$	- The same rate of cooling as sample series 2, only tempering at $25^{\circ}\mathrm{C}$ for two hours.
Sample series 4, $15^{\circ} \rightarrow 0^{\circ}\mathrm{C}$	- The melted milk fat cooled at $15^{\circ}\mathrm{C}$ for two hours, then at $0^{\circ}\mathrm{C}$ overnight.
Sample series 5, $25^{\circ} \rightarrow 0^{\circ}\mathrm{C}$	- The melted milk fat cooled at $25^{\circ}\mathrm{C}$ for two hours, then at $0^{\circ}\mathrm{C}$ overnight.

Mean values of the coefficients of thermal expansion were:

Winter milk fat

$\alpha_s = 0.582 \times 10^{-3}\ \mathrm{cm^3/g\ ^{\circ}C}$

$\alpha_l = 0.882 \times 10^{-3}\ \mathrm{cm^3/g\ ^{\circ}C}$

Summer milk fat

$\alpha_s = 0.608 \times 10^{-3}\ \mathrm{cm^3/g\ ^{\circ}C}$

$\alpha_l = 0.879 \times 10^{-3}\ \mathrm{cm^3/g\ ^{\circ}C}$

Geometric or logarithmic means of these values were i~~n~~dentical with above-mentioned means.

Standard deviations of a normal distribution by the least squares method of the coefficients of thermal expansion were:

Winter milk fat

$$\sigma_s = 0.0098 \times 10^{-3}$$
$$\sigma_l = 0.0071 \times 10^{-3}$$

Summer milk fat

$$\sigma_s = 0.0084 \times 10^{-3}$$
$$\sigma_l = 0.0045 \times 10^{-3}$$

The coefficients of variability of these values, i.e., the standard deviation, as per cent of the mean value, were:

Winter milk fat

$$V_s = 1.68\%$$
$$V_l = 0.80\%$$

Summer milk fat

$$V_s = 1.38\%$$
$$V_l = 0.51\%$$

The melting dilation

The melting dilation is the expansion value for an isothermal change from the solid to the liquid state. The melting dilations were found as differences between volumes on "solid" and "liquid" lines. The melting dilation of winter and summer milk fat for each thermal treatment was calculated and also the mean value of replicates for each thermal treatment. In Table 3, the melting dilations of winter and summer milk fat, for the temperature range from -40° to 40°C, are given. For winter milk fat, the melting dilation at -40°C was 47.53×10^{-3} cm^3/g;

at 40°C, 71.40 x 10^{-3} cm^3/g; and for summer milk fat, 45.46 x 10^{-3} cm^3/g and 67.71 x 10^{-3} cm^3/g with the average rate of increase being 0.30 x 10^{-3} cm^3/g °C for winter, and 0.28 x 10^{-3} cm^3/g °C for summer milk fat.

The solid fat content

The solid fat content of winter and summer milk fat was determined over the temperature range in which the fat is plastic, in this case, -40° to 40°C. Using the coefficients of thermal expansion of the solid and liquid phases, the volumes on "solid" and "liquid" lines were calculated for each five-degree interval. The "solid" and "liquid" lines, obtained as described, were used for the calculations of solid fat content for the given temperature range. In Fig. 3, the dilatometric curve for winter milk fat and thermal treatment $0° \rightarrow 25°C$ is given. Fig. 4 represents the dilatometric curve of summer milk fat for the same thermal treatment. In Figs. 3 and 4, the equations for the "solid" and "liquid" lines are given, which are calculated as regression lines using the data of measurements in the regions where the fat was completely solid (-40° to -60°C) and completely liquid (40° to 60°C). In Tables 4 and 5, the solid fat contents of winter and summer milk fat and different thermal treatments are listed.

The rate of melting

Figs. 5 - 9 represent solid fat content and rate of melting of winter milk fat for each thermal treatment, and Figs. 10 - 14 represent solid fat content and rate of melting of summer milk fat.

In these figures, curves A represent the change of solid fat content with temperature, and curves B are derivative curves representing the average slope (in % per ^{o}C) of the basic curves A between two temperatures. The physical expression of the derivative curve can be easily seen from its dimension, i.e. per cent per degree centigrade which represents the rate of melting. The horizontal dotted lines C represent the average rate of melting over the entire range. In Tables 6 and 7 the numerical values for rate of melting are listed for each thermal treatment of winter and summer milk fat.

In Tables 8 and 9 several characteristic values of the rate of melting of winter and summer milk fat and different thermal treatments are given. These are: the overall average rate of melting which is naturally constant and independent of thermal treatments, the above average rate of melting which is defined as an average rate of melting in the temperature interval limited by the intersections of the rate-of-melting curve (B, Figs. 5 - 14) and overall average rate of melting (horizontal line C), the third characteristic value of rate of melting is its maximum and the corresponding temperature. In Table 10 a comparison of the rates of melting with different thermal treatments of winter and summer milk fat is given.

Table 1. The coefficients of thermal expansion of winter milk fat

Coefficient of thermal expansion	N° of sample	Thermal treatment				
		1	2	3	4	5
		10^{-3} cm^3/g °C				
α_s	1	0.588	0.584	0.584	0.590	0.567
	2	0.588	0.572	0.576	0.586	0.563
	3	0.594	0.588	0.588	0.588	0.570
	4	0.598	0.580	0.580	0.590	0.567
α_l	1	0.880	0.878	0.882	0.894	0.884
	2	0.888	0.884	0.884	0.876	0.874
	3	0.890	0.884	0.888	0.884	0.876
	4	0.879	0.874	0.872	0.880	0.888

α_s = Coefficient of thermal expansion of solid phase

α_l = Coefficient of thermal expansion of liquid phase

Table 2. The coefficients of thermal expansion of summer milk fat

Coefficient of thermal expansion	N° of sample	Thermal treatment				
		1	2	3	4	5
		10^{-3} cm^3/g °C				
α_s	1	0.608	0.612	0.610	0.612	0.620
	2	0.604	0.624	0.598	0.588	0.610
	3	0.616	0.618	0.616	0.600	0.608
	4	0.610	0.602	0.602	0.602	0.608
α_l	1	0.882	0.882	0.882	0.878	0.888
	2	0.876	0.874	0.880	0.870	0.874
	3	0.874	0.880	0.882	0.874	0.880
	4	0.879	0.882	0.878	0.888	0.880

α_s = Coefficient of thermal expansion of solid phase

α_l = Coefficient of thermal expansion of liquid phase

Table 3. The melting dilation of winter and summer milk fat

Temperature °C	Winter	Summer
	10^{-3} cm^3/g °C	
-40	47.53	45.46
-35	49.03	46.84
-30	50.52	48.17
-25	52.02	49.57
-20	53.50	50.89
-15	54.99	52.27
-10	56.49	53.63
- 5	57.98	54.97
0	59.47	56.33
5	60.96	57.70
10	62.45	59.06
15	63.94	60.91
20	65.44	62.28
25	66.93	63.51
30	68.42	64.99
35	69.91	66.35
40	71.40	67.71

Table 4. The solid fat content of winter milk fat with various thermal treatments

Thermal treatment	1	2	3	4	5
Temperature °C	Solid fat content %				
-40	99.4	99.2	99.3	99.5	99.4
-35	97.8	97.9	97.6	97.7	98.4
-30	95.5	95.1	94.9	95.6	95.8
-25	91.3	90.7	91.1	92.0	91.2
-20	86.0	85.7	86.4	86.8	85.5
-15	80.6	80.6	81.1	81.3	80.2
-10	76.0	75.5	75.5	76.1	76.0
- 5	72.9	70.4	69.4	71.3	72.2
0	69.9	65.0	62.4	66.5	68.8
5	66.5	58.5	53.9	60.9	64.4
10	61.9	49.9	43.6	51.2	58.3
15	45.2	39.0	32.2	37.7	43.2
20	23.3	24.4	20.9	23.2	23.1
25	15.1	14.1	12.7	14.9	14.4
30	8.6	7.9	7.0	8.0	7.6
35	2.6	2.5	2.4	2.5	2.5
40	0	0	0	0	0

Table 5. The solid fat content of summer milk fat with various thermal treatments

Thermal treatment	1	2	3	4	5
Temperature °C	Solid fat content %				
-40	99.8	99.7	99.7	99.7	99.5
-35	98.4	98.1	98.6	98.2	97.8
-30	96.0	95.2	95.2	95.8	95.4
-25	91.9	91.0	90.8	92.2	91.6
-20	86.6	84.9	85.5	86.6	86.7
-15	80.6	78.7	79.4	80.1	80.9
-10	75.8	73.4	72.4	74.5	75.7
- 5	71.9	67.5	64.9	68.5	71.2
0	68.4	60.7	57.0	61.7	67.3
5	64.0	52.9	48.9	54.2	62.4
10	55.0	43.7	40.1	45.7	53.2
15	39.9	32.4	30.1	32.5	39.1
20	20.2	19.7	19.0	19.2	20.2
25	12.6	12.3	11.2	12.2	12.3
30	6.6	6.4	5.8	6.7	6.2
35	1.2	1.9	1.5	2.1	1.8
40	0	0	0	0	0

Table 6. The rate of melting of winter milk fat with various thermal treatments

Thermal treatment		1	2	3	4	5
Temperature °C from	to	Rate of melting %/5°C				
-40	-35	1.6	1.3	1.7	1.8	1.0
-35	-30	2.3	2.8	2.7	2.1	2.6
-30	-25	4.2	4.4	3.8	3.6	4.6
-25	-20	5.3	5.0	4.7	5.2	5.7
-20	-15	5.4	5.1	5.3	5.5	5.3
-15	-10	4.6	5.1	5.6	5.2	4.2
-10	- 5	3.1	5.1	6.1	4.8	3.8
- 5	0	3.0	5.4	7.0	4.8	3.4
0	5	3.4	6.5	8.5	5.6	4.4
5	10	4.6	8.6	10.3	9.7	6.1
10	15	16.7	10.9	11.4	13.5	15.1
15	20	21.9	14.6	11.3	14.5	20.1
20	25	8.2	10.3	8.2	8.3	8.7
25	30	6.5	6.2	5.7	6.9	6.8
30	35	6.0	5.4	4.6	5.5	5.1
35	40	2.6	2.5	2.4	2.5	2.5

Table 7. The rate of melting of summer milk fat with various thermal treatments

Thermal treatment		1	2	3	4	5
Temperature °C		Rate of melting %/5°C				
from	to					
-40	-35	1.4	1.6	1.1	1.5	1.7
-35	-30	2.4	2.9	3.4	2.4	2.4
-30	-25	4.1	4.2	4.4	3.6	3.8
-25	-20	5.3	6.1	5.3	5.6	4.9
-20	-15	6.0	6.2	6.1	6.5	5.8
-15	-10	4.8	5.3	7.0	5.6	5.2
-10	- 5	3.9	5.9	7.5	6.0	4.5
- 5	0	3.5	6.8	7.9	6.8	3.9
0	5	4.4	7.8	8.1	7.5	4.9
5	10	9.0	9.2	8.8	8.5	9.2
10	15	15.1	11.3	10.0	13.2	14.1
15	20	19.7	12.7	11.1	13.3	18.9
20	25	7.6	7.4	7.8	7.0	7.9
25	30	6.0	5.9	5.4	5.5	6.1
30	35	5.4	4.5	4.3	4.6	4.4
35	40	1.2	1.9	1.5	2.1	1.8

Table 8. Characteristic values of the rate of melting of winter milk fat

Thermal treatment		1	2	3	4	5
The average rate of melting 1.14 %/°C - for all thermal treatments						
The above average rate of melting						
Temperature interval	from	8.5	-0.4	-11.7	2.6	6.8
	to	33.4	30.9	28.1	32.5	30.9
Rate of melting %/°C		2.40	1.89	1.72	1.95	2.34
Maximum rate of melting						
Temperature °C		16.5	17.5	15.4	15.9	16.3
Rate of melting %/°C		4.44	3.00	2.36	3.04	4.16

Table 9. Characteristic values of the rate of melting of summer milk fat

Thermal treatment		1	2	3	4	5
The average rate of melting						
1.14 %/°C - for all thermal treatments						
The above average rate of melting						
Temperature interval	from	4.6	-8.2	-20.0	-10.2	3.7
	to	29.6	28.1	26.6	26.9	29.0
Rate of melting %/°C		2.30	1.74	1.64	1.74	2.22
Maximum rate of melting						
Temperature °C		16.8	16.5	16.3	14.6	17.6
Rate of melting %/°C		4.00	2.60	2.28	2.96	3.80

Table 10. Comparison of rates of melting with various thermal treatments

Thermal treatment		1	2	3	4	5
		Average rate of melting of winter milk fat %/°C				
Temperature interval	0° - 25°C	2.19	2.04	1.91	2.06	2.18
	10° - 20°C	3.86	2.55	2.27	2.80	3.52
		Average rate of melting of summer milk fat %/°C				
Temperature interval	0° - 25°C	2.23	1.94	1.83	1.98	2.20
	10° - 20°C	3.48	2.40	2.11	2.65	3.30

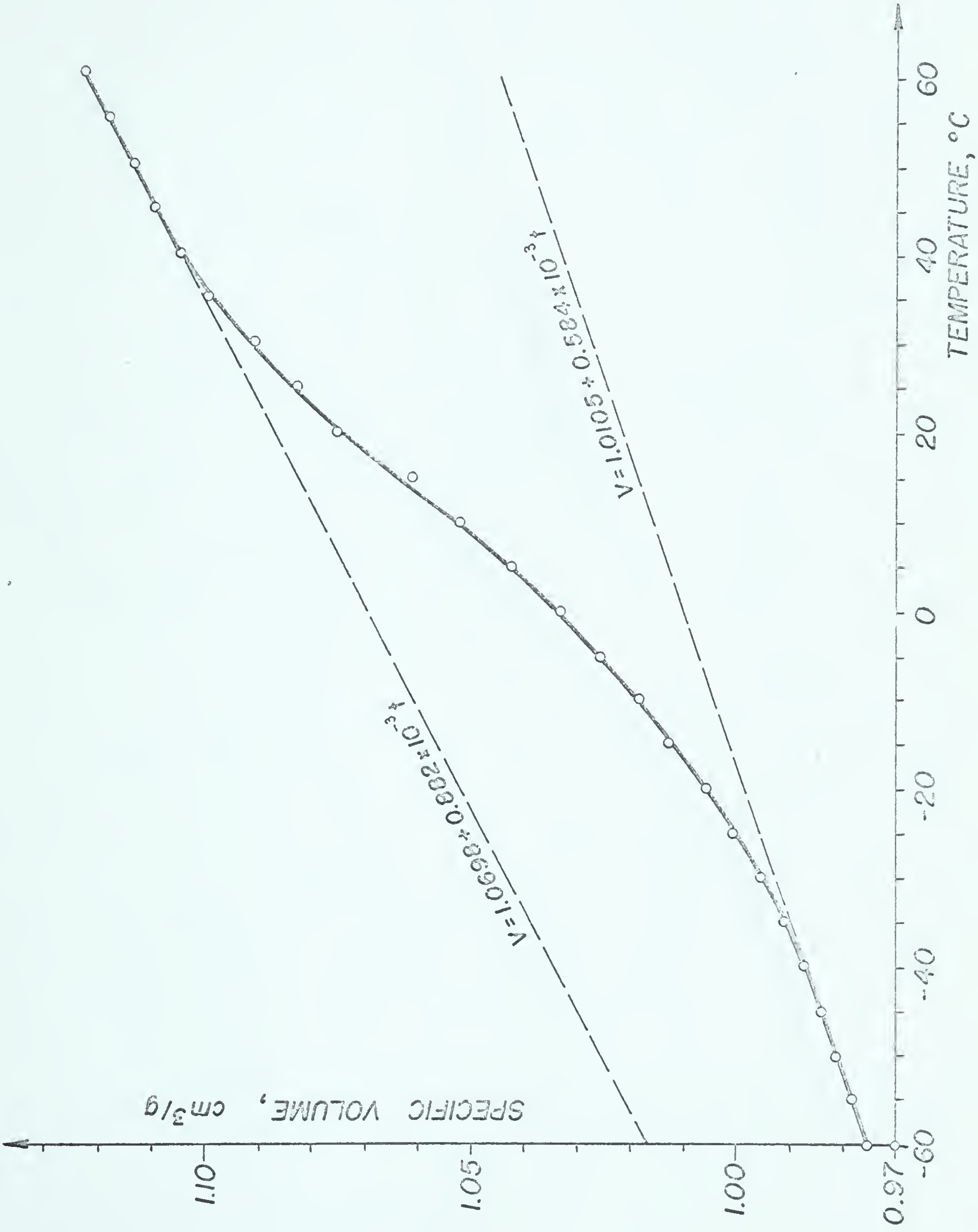

Fig. 3. The dilatometric curve of winter milk fat, sample series 3

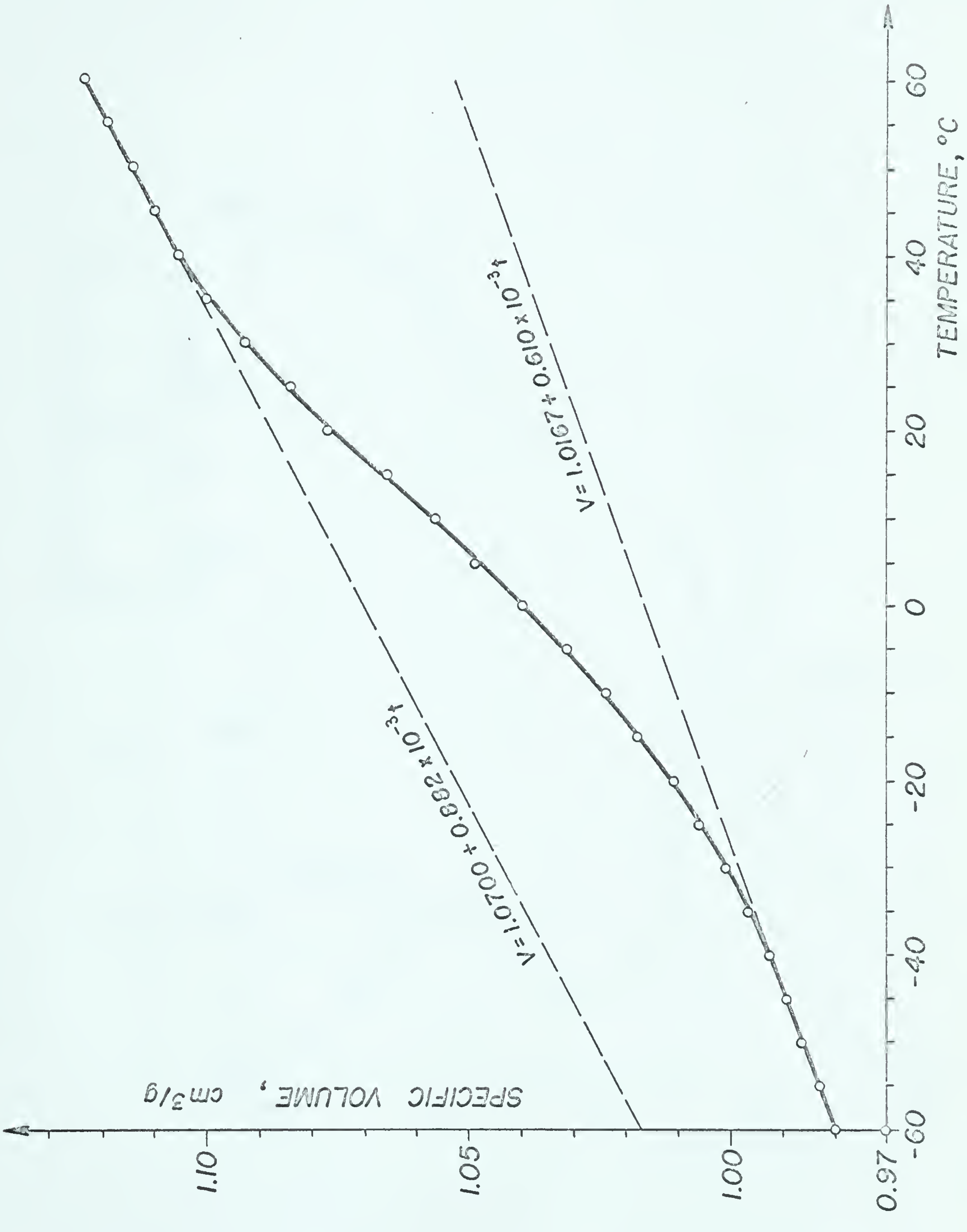

Fig. 4. The dilatometric curve of summer milk fat, sample series 3

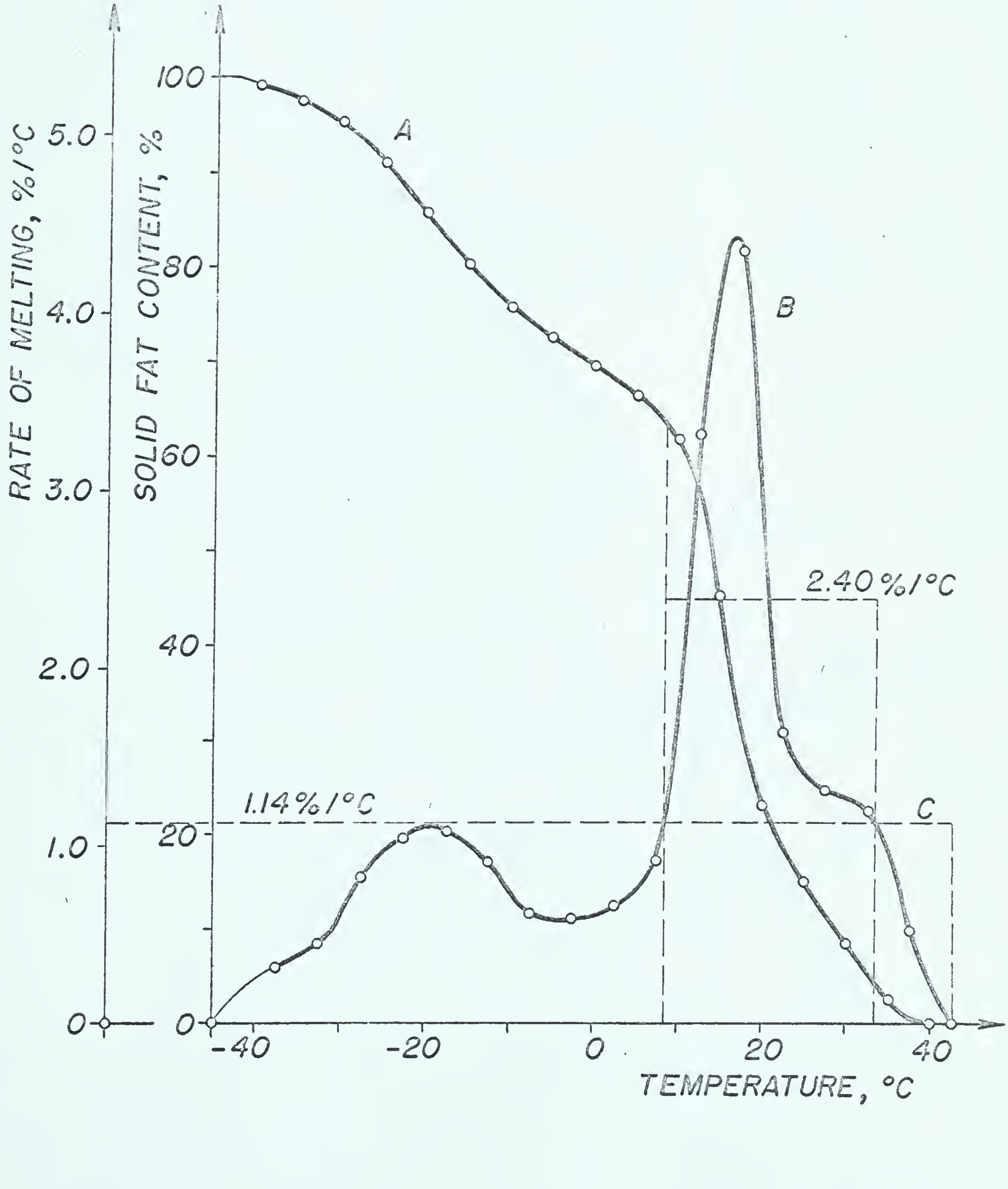

Fig. 5. The solid fat content and the rate of melting, winter milk fat, sample series 1

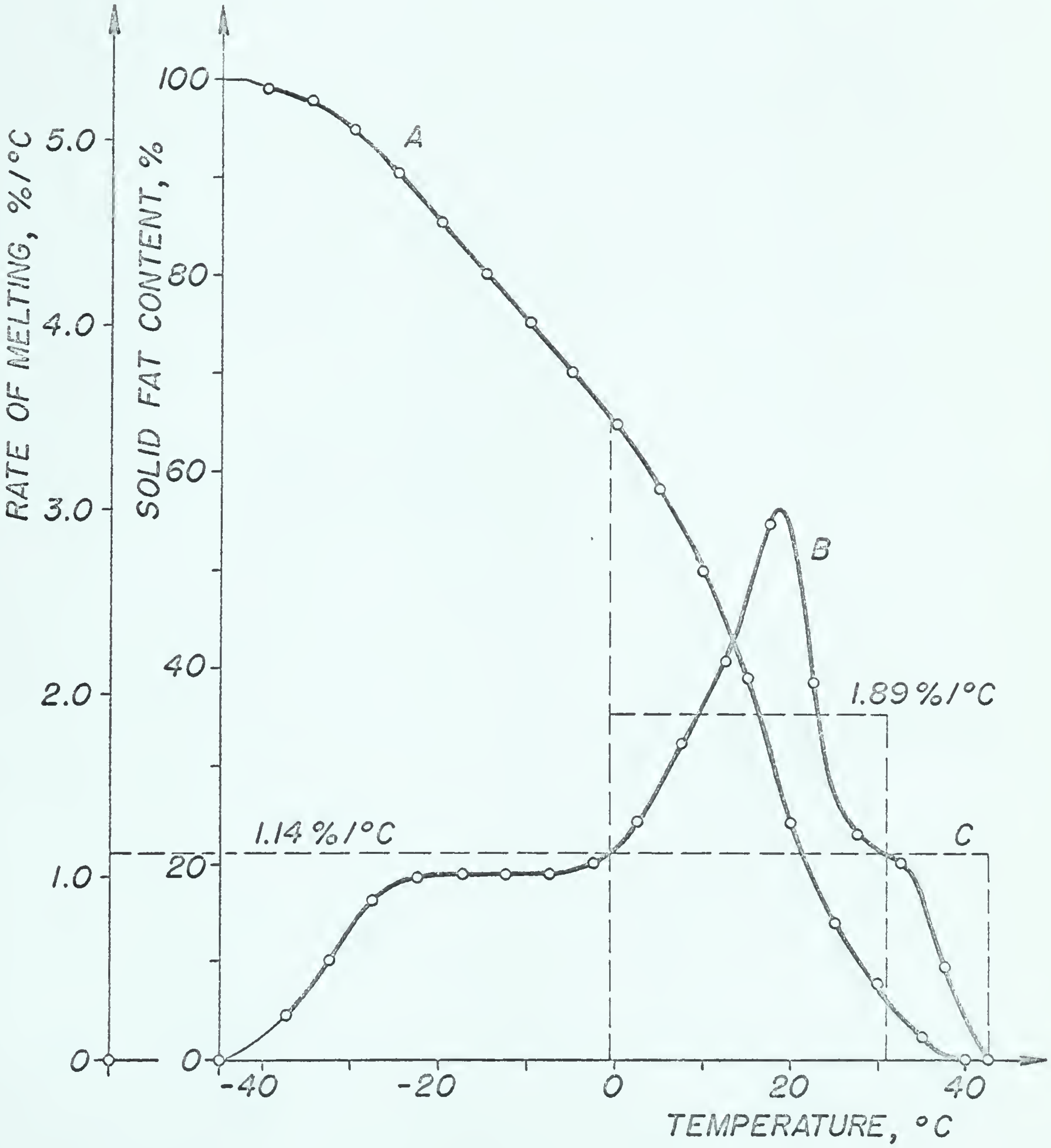

Fig. 6. The solid fat content and the rate of melting, winter milk fat, sample series 2

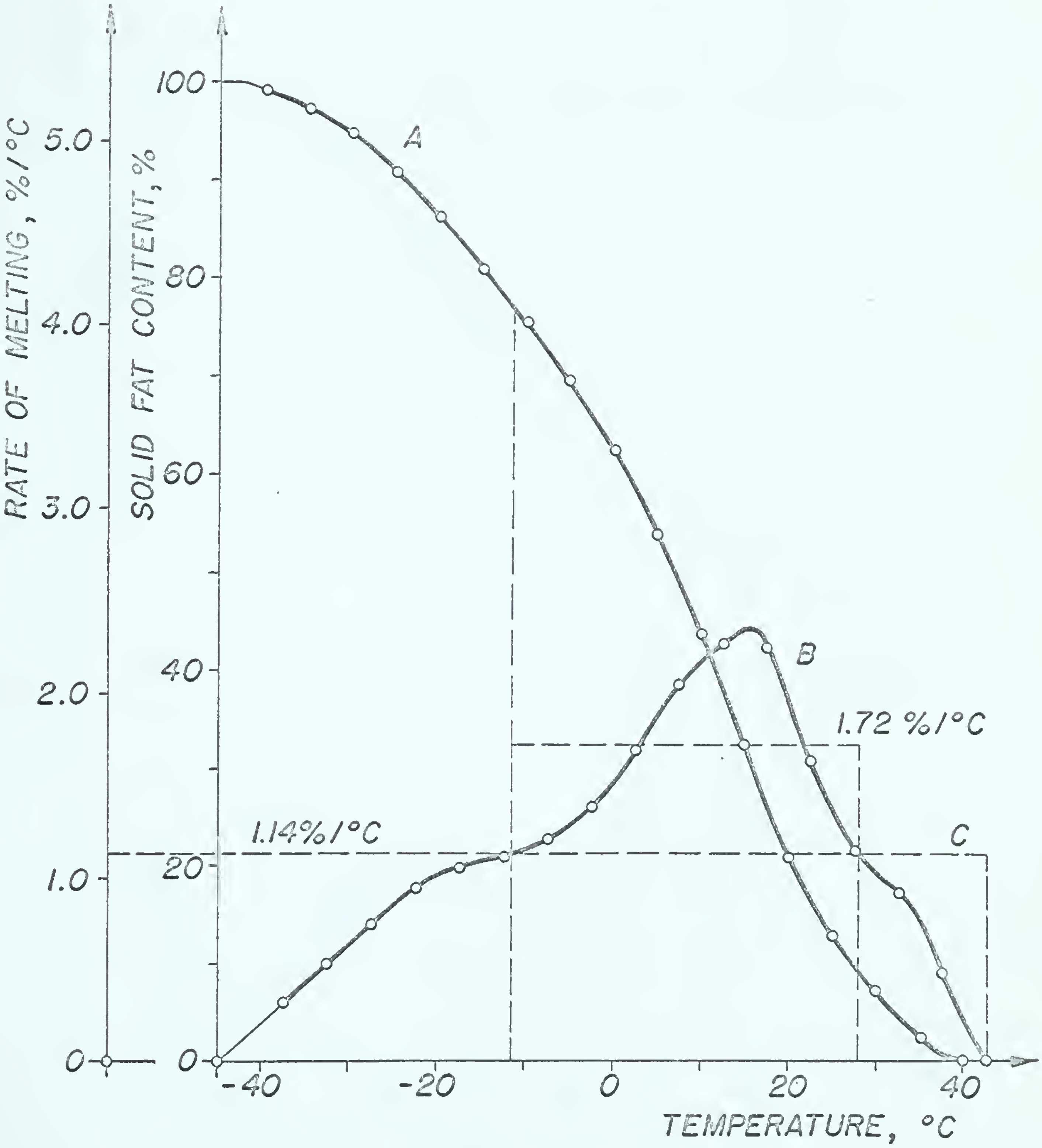

Fig. 7. The solid fat content and the rate of melting, winter milk fat, sample series 3

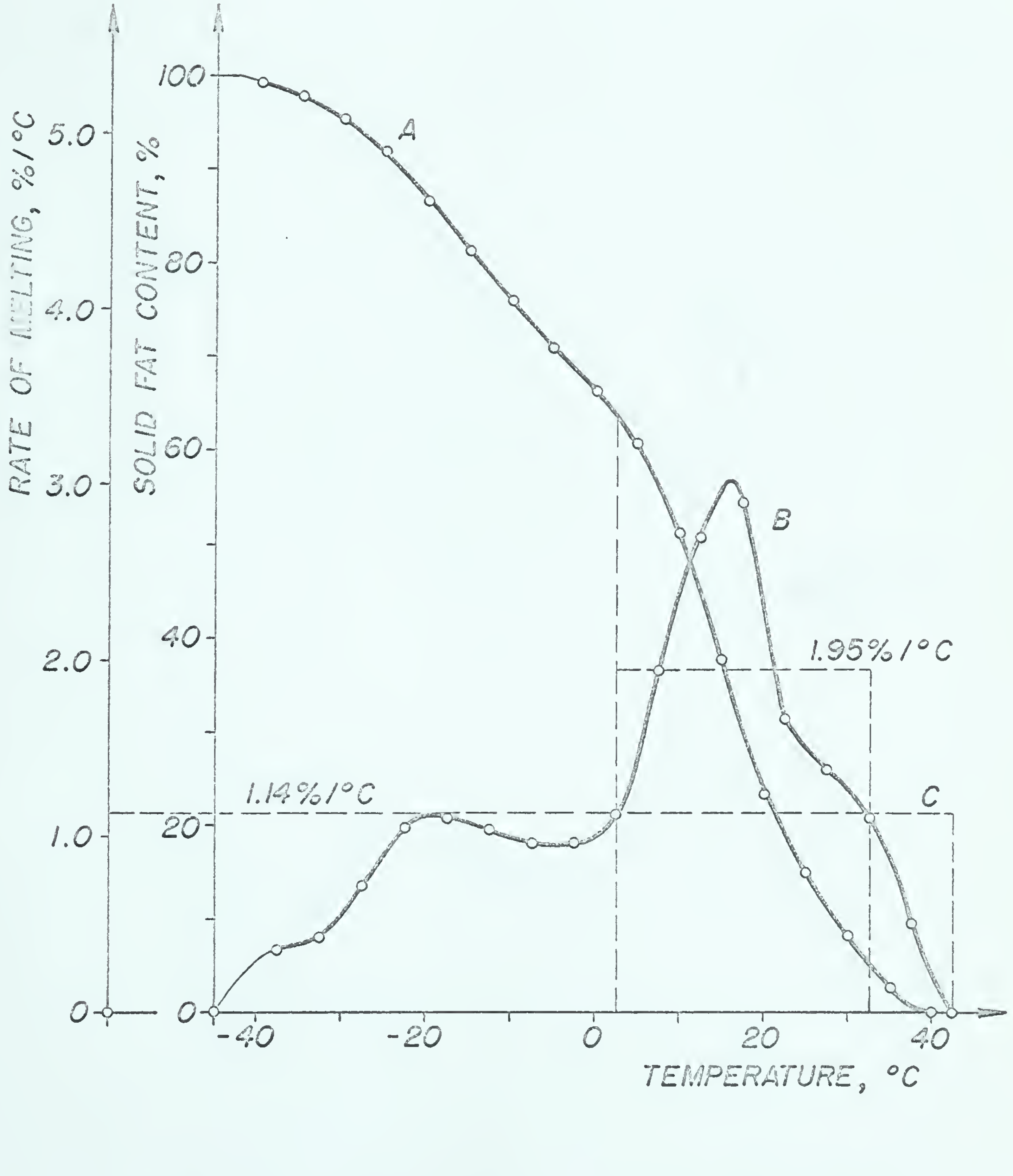

Fig. 8. The solid fat content and the rate of melting, winter milk fat, sample series 4

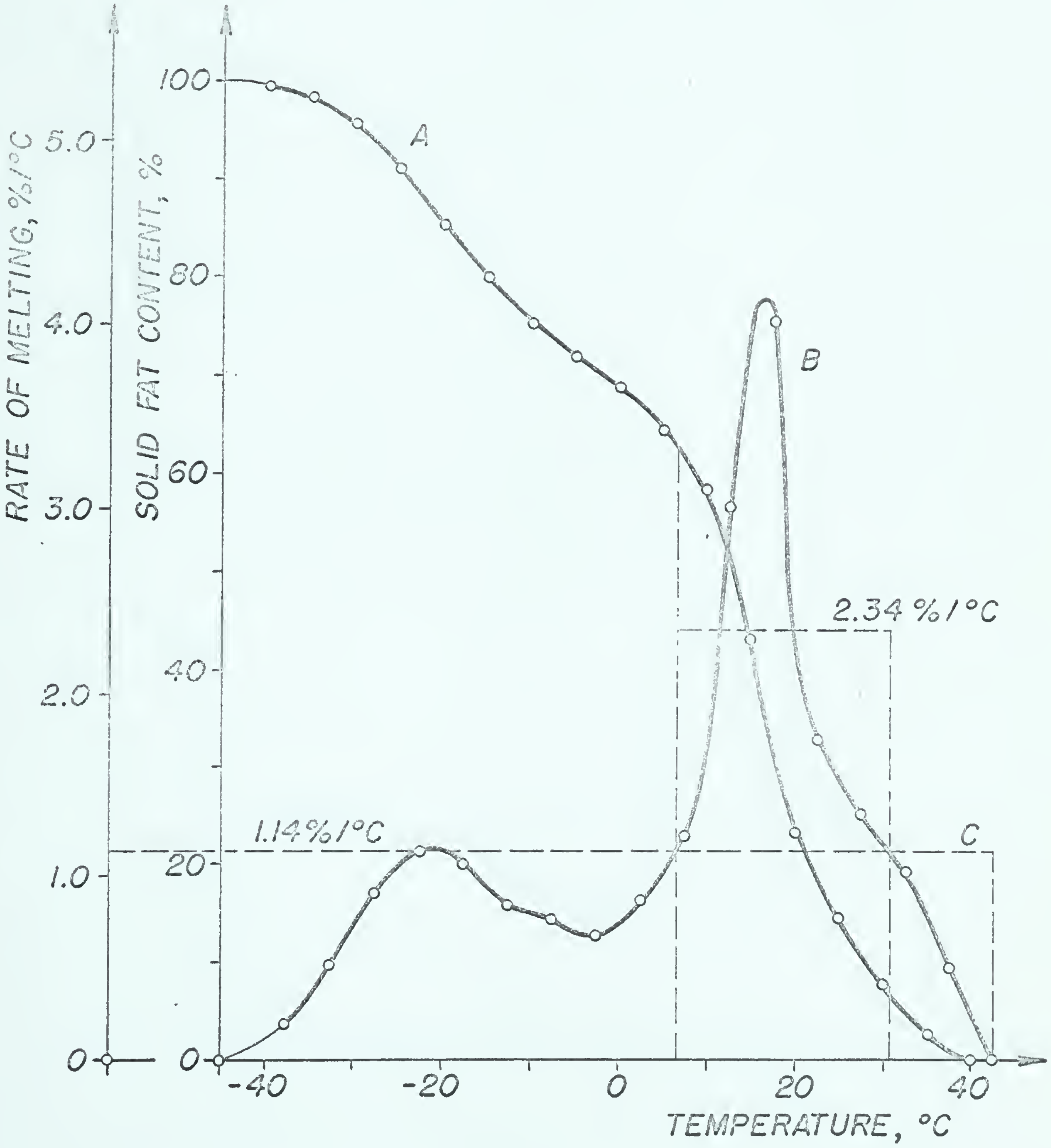

Fig. 9. The solid fat content and the rate of melting, winter milk fat, sample series 5

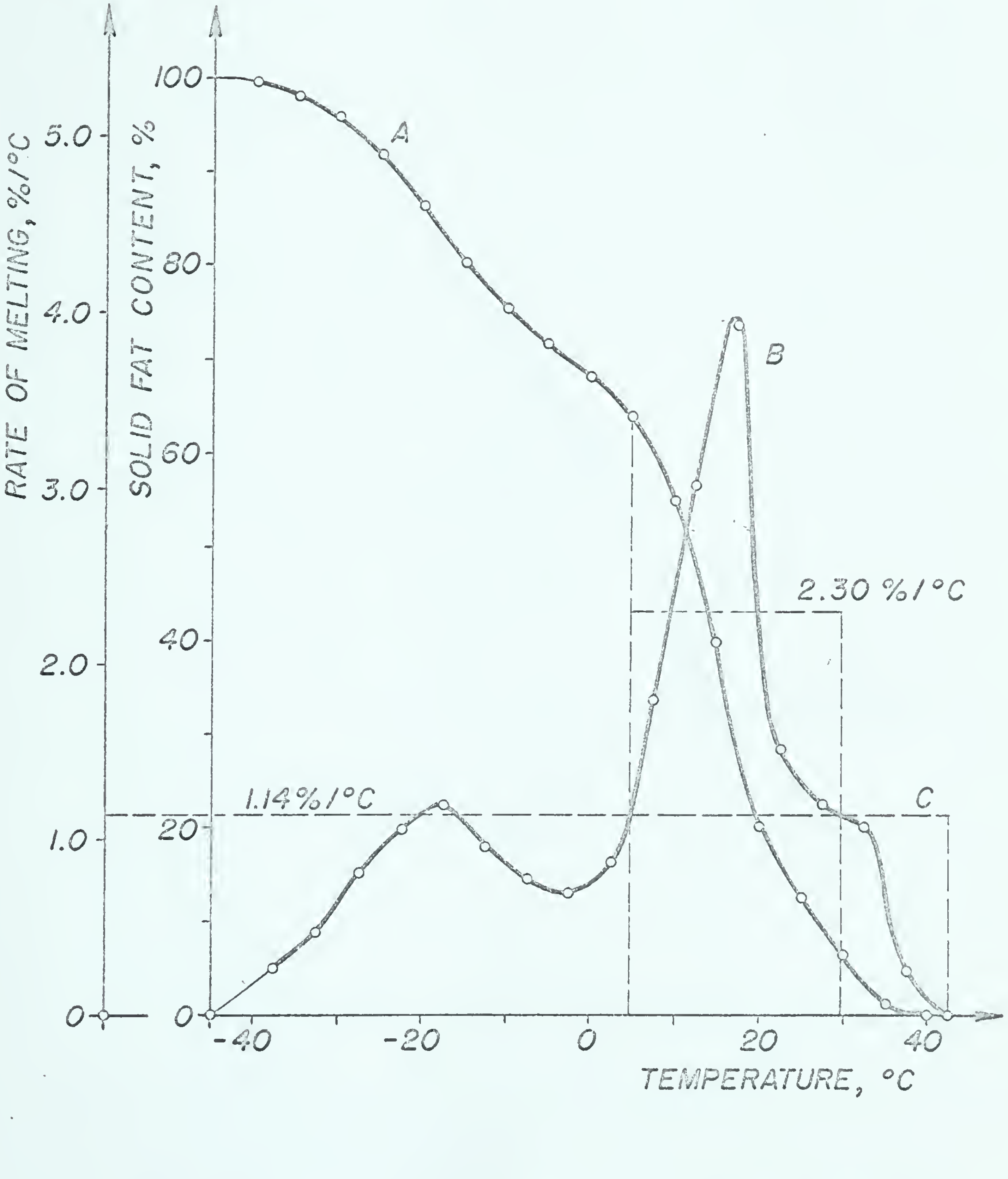

Fig. 10. The solid fat content and the rate of melting, summer milk fat, sample series 1

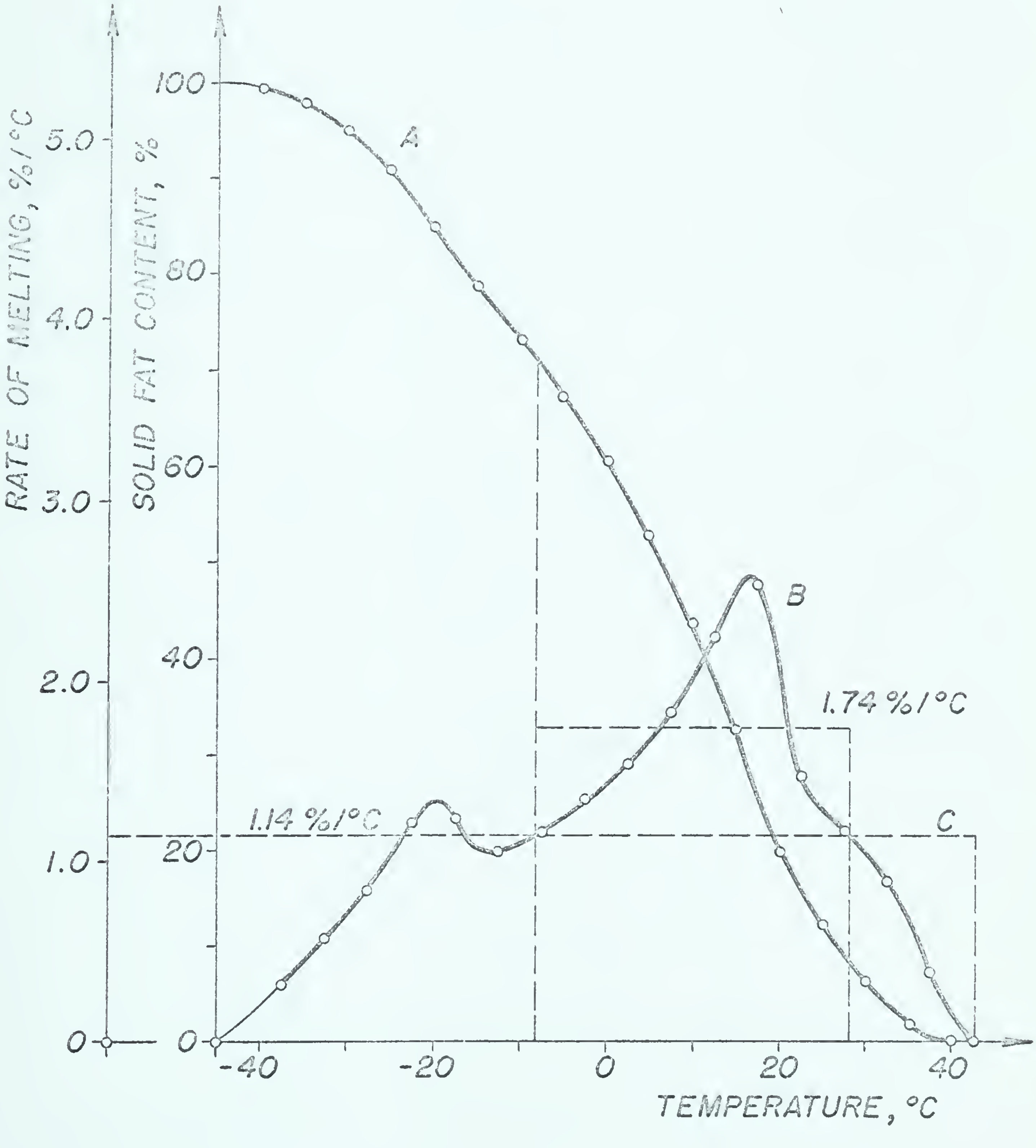

Fig. 11. The solid fat content and the rate of melting, summer milk fat, sample series 2

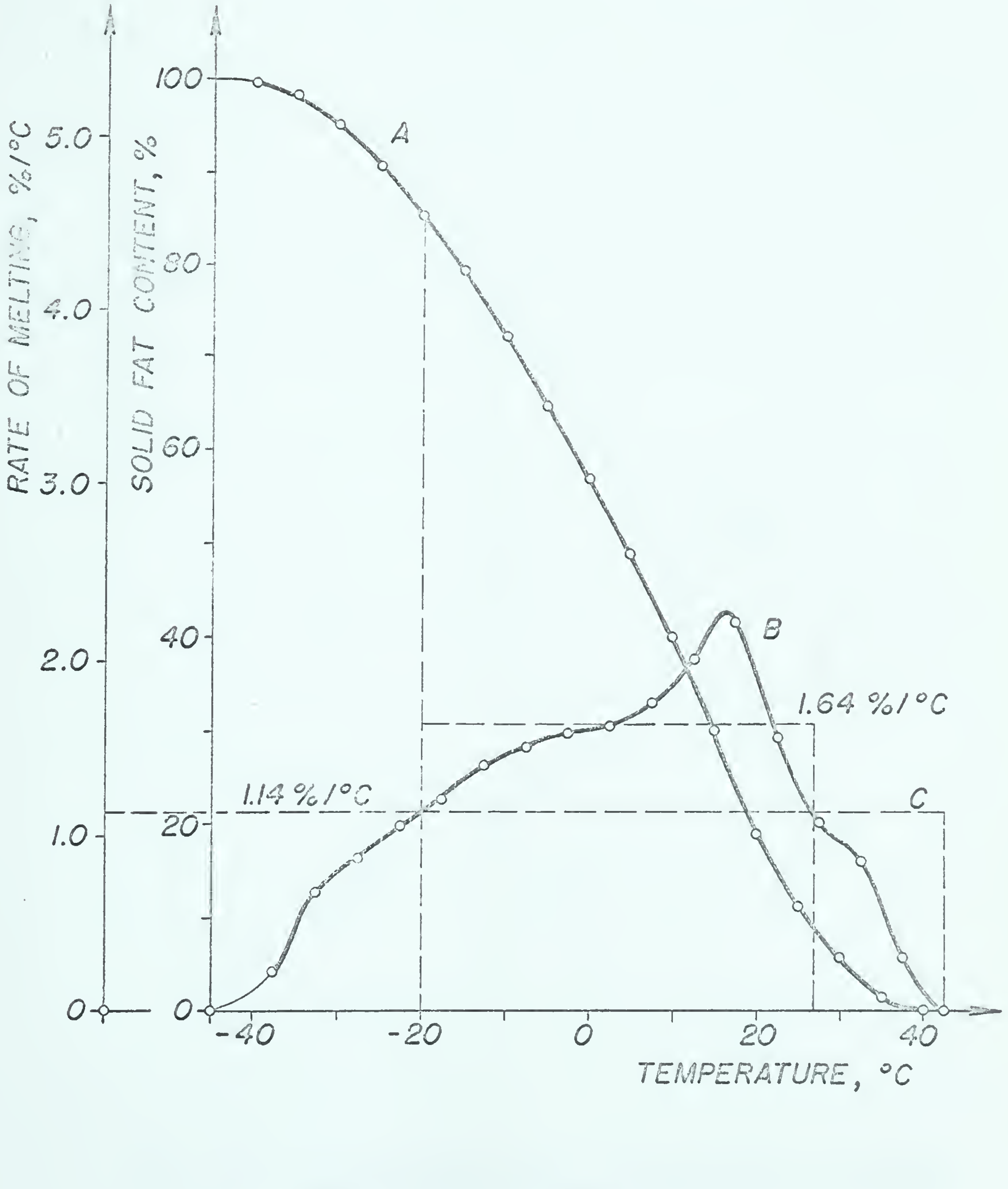

Fig. 12. The solid fat content and the rate of melting, summer milk fat, sample series 3

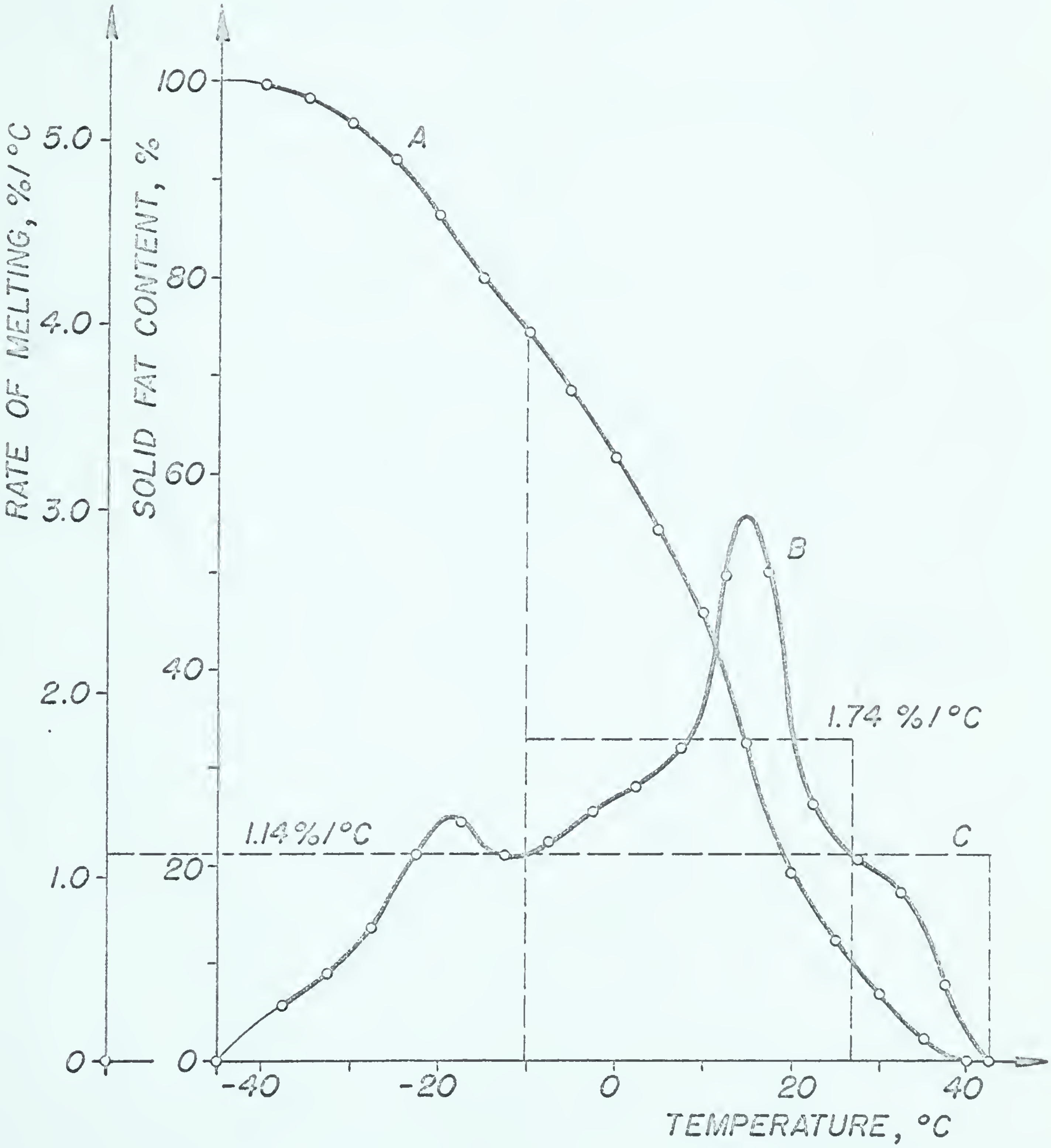

Fig. 13. The solid fat content and the rate of melting, summer milk fat, sample series 4

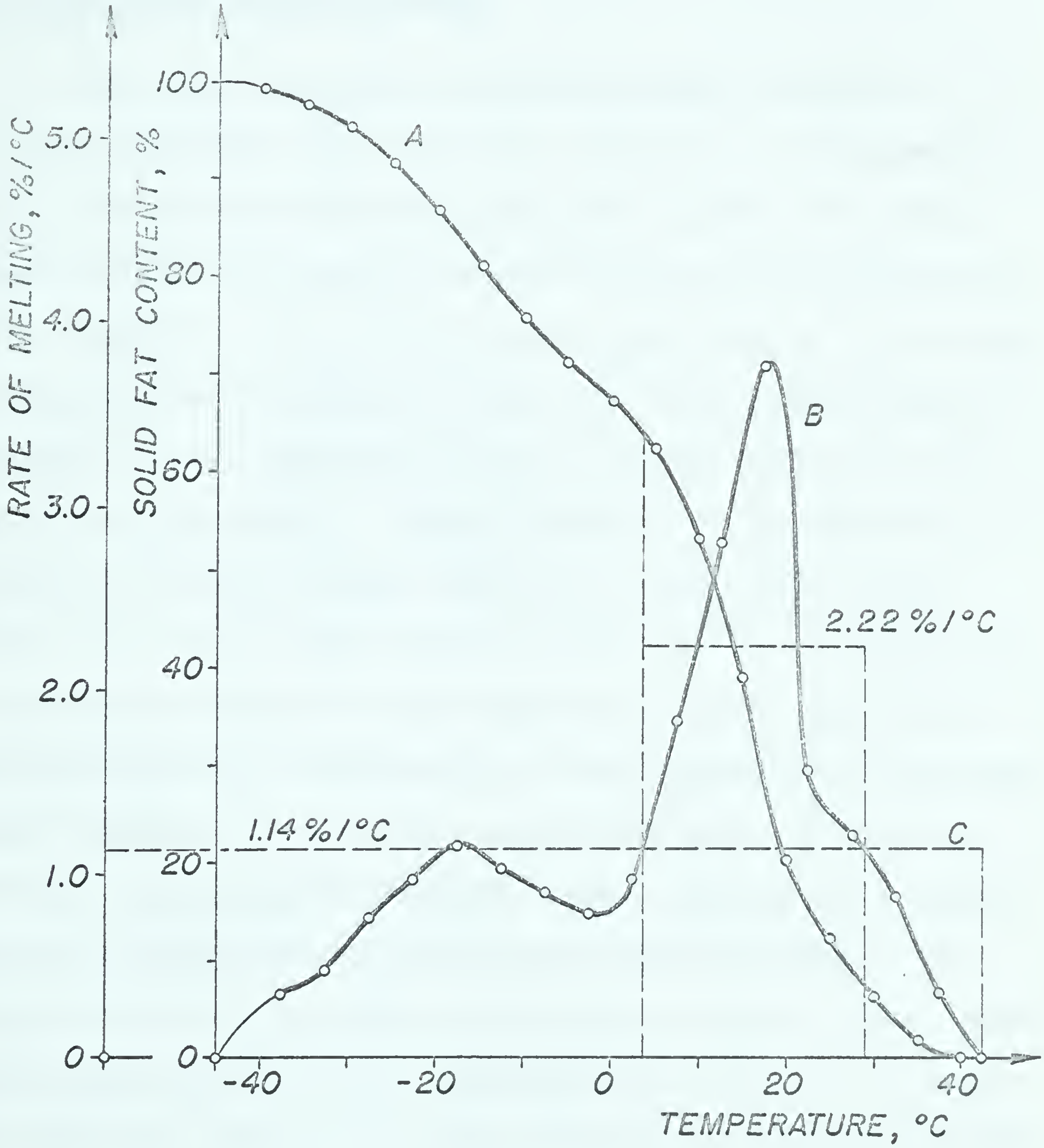

Fig. 14. The solid fat content and the rate of melting, summer milk fat, sample series 5

DISCUSSION

The coefficient of thermal expansion

The thermal expansion of the liquid phase of milk fat was found to be higher than that of the solid phase, a finding which has also been reported by several authors (18, 38, 83). It could be assumed that different thermal treatments influence the coefficients of thermal expansion of the solid fat because they result in the formation of different types of crystals and these could have different spatial arrangements in the completely solid fat. For this reason, the data was analyzed statistically. Standard deviations of the normal distribution for different thermal treatments of winter milk fat were 0.0179×10^{-3}, and of summer milk fat, 0.0045×10^{-3}, with coefficients of variability 3.076% and 0.740%, respectively. These figures show that the differences in coefficients of thermal expansion for different thermal treatments were within the experimental error. In addition, there were only negligible differences between coefficients of thermal expansion of liquid milk fat for different thermal treatments. The standard deviation of the normal distribution for various thermal treatments of winter milk fat in the liquid state was 0.0045×10^{-3}, and of summer milk fat, 0.0045×10^{-3}, with coefficients of variability 0.510% and 0.512%, respectively. It can be concluded that the coefficients of thermal expansion of milk fat do not differ significantly after various thermal treatments.

The melting dilation

Measurements of the thermal dilation of milk fat have shown that there are three distinct temperature regions in which milk fat has different characteristics. Below -40°C, the fat is completely solid; between -40°C and 40°C, the fat is plastic, i.e., it contains solid and liquid phase simultaneously in a ratio which is, besides other factors, chiefly dependent on temperature; above 40°C, the fat is completely liquid and shows the properties of Newtonian fluids.

In the region where milk fat is plastic, an increase in temperature influences the thermal dilation of the solid phase, the thermal dilation of liquid phase, and the melting dilation. Because, as is shown above, the thermal dilation of completely solid and completely liquid fat is regular, only the plastic region will be dealt with here.

It was found that various thermal treatments which were used did not influence the melting dilation of milk fat. Certain differences between melting dilations of winter and summer milk fat were found. Winter milk fat had a greater melting dilation than summer milk fat as a consequence of a higher solid fat content of winter milk fat.

The solid fat content and the rate of melting

In the work presented, several thermal treatments were used. The main idea was to apply different cooling procedures resulting in different conditions for milk fat crystallization. The temperature treatment of sample series 1 ($0^{\circ} \rightarrow 0^{\circ}C$) provided the maximum rate of cooling. The 2nd and 3rd sample series received the same rate of cooling.

but a certain degree of recrystallization was obtained by tempering at 15° and 25°C. In the case of sample series 4 and 5, the cooling was divided into two steps, so-called stepwise cooling. In sample series 4, the first step was cooling to 15°C, resulting in the formation of a certain amount of layer crystals, followed by cooling to 0°C. Sample series 5 was first cooled to 25°C and then to 0°C. The temperature 0°C was used as the lowest one for all thermal treatments because, as was pointed out before (18), cooling to lower temperatures does not influence the solid fat content.

As can be seen from Tables 4 and 5, there were no great differences in solid fat content in the range of -40° to 0°C after different thermal treatments. Also, there were no great differences in solid fat content at temperatures above 25°C. Thus, the greatest differences in the solid fat content occurred between 0° and 25°C. For the above-mentioned temperatures there were higher solid fat contents in winter milk fat after various thermal treatments than in summer milk fat.

Generally, rapid cooling to 0°C resulted in higher solid fat content than stepwise cooling and tempering. If rapidly-cooled milk fat (sample series 1) is taken as a reference, then sample series 5 (stepwise cooling 25° → 0°C) showed the greatest similarity. This seems quite logical because by cooling to 25°C, only about 14% of the fat was crystallized with a lower rate of cooling, while most of the remaining 86% had been crystallized in the second step, during cooling from 25° to 0°C with a high rate of cooling. Greater differences in solid fat content appeared between the reference sample series and sample

series 2 and 4. The temperature of 15°C seems to be a critical one for milk fat, because in the proximity of this temperature a large proportion of the crystals melt and in both cases (tempering at 15°C, and stepwise cooling with the first step at 15°C), 15°C is involved as a key temperature. Sample series 3 (0° → 25°C) shows the greatest difference with the reference sample series in the temperature interval 0° - 25°C. It is clear from these results that thermal treatment has a marked influence on the solid fat content of both winter and summer milk fat.

The horizontal line C, (Figs. 5 - 14) showing the value of 1.14%/°C, represents the average rate of melting over the entire temperature range in which the milk fat is plastic. The temperature range, in which the rate of melting is above average (1.14%/°C) depends on the thermal treatment as well as on the chemical composition of the fat.

For winter milk fat, the reference sample series (rapid cooling to 0°C) has the narrowest temperature range in which above average amounts of crystals melt, from 8.5° to 33.4°C. The decrease in solid fat content, within this range, is $63.8 - 4.1 = 59.7\%$, which gives a rate of melting of $59.7/24.9 = 2.40\%/^{\circ}C$. Sample series 5 is only slightly different $(62.7 - 6.3)/(30.9 - 6.8) = 2.34\%/^{\circ}C$. A considerably wider range was found with both sample series 2 and 4, -0.4° to 30.9°C, and 2.6° to 32.5°C; decreases in solid fat contents being $65.2 - 6.0 = 59.2\%$, and $63.5 - 5.2 = 58.3\%$, respectively with a rate of melting of 1.89 and 1.95%/°C. Sample series 3 showed the greatest deviation from the reference sample series, with above average

melting between -11.7° and 28.1°C, and decrease in the solid fat content of 77.4 - 9.0 = 68.4% and rate of melting of 1.72%/°C.

For summer milk fat, the values of melting rates for the various thermal treatments were similar to those of winter milk fat. Sample series 1 had a rate of melting of 2.30%/°C and sample series 5, 2.22%/°C. Sample series 2, 3, and 4 were 1.74, 1.64, and 1.74%/°C respectively. However, the temperature intervals in which above average melting rates occur, were wider than of winter milk fat, which indicates that summer milk fat has a greater variety of crystals with melting points that differ from each other over a wider range than winter milk fat.

In order to provide a possibility for direct comparison of melting behaviour of milk fat thermally treated in different ways, two fixed temperature ranges were chosen: 0° - 25°C and 10° - 20°C. The limits of the first temperature interval were chosen because the solid fat content changes most between 0°C and 25°C. The interval from 10° - 20°C was used because the maximum rate of melting occurs between 14.6° and 17.6°C. From table 10, it can be concluded that average rates of melting within the two fixed temperature ranges for both winter and summer milk fat, and for different thermal treatments, are in agreement with the average rates of melting given in Tables 8 and 9.

The highest solid fat content in winter and summer milk fat was found in sample series 1, a similar conclusion was reached in several published papers (20, 21, 24, 26, 28). The rates of melting indicate that the maximum amount of mixed crystals was formed by rapid cooling to 0°C (sample series 1). The presence of mixed crystals means

that the greatest part of the fat will melt in a narrow temperature range, i.e., with a high rate of melting. The slightly lower solid fat content in sample series 5 can be explained by assuming that by holding at 25°C for two hours, a certain amount of high-melting glycerides was crystallized, thus diminishing the number of centers of crystallization. Sample series 3 ($0^\circ \rightarrow 25^\circ C$) shows the opposite results from sample series 1 and 5, i.e., the lowest solid fat content and the lowest rate of melting. Tempering at 25°C, for two hours, resulted in a partial recrystallization, so that some of the previously formed mixed crystals were transformed into layer crystals. Sample series 2 ($0^\circ \rightarrow 15^\circ C$) and 4 ($15^\circ \rightarrow 0^\circ C$) differed slightly from each other. The solid fat content and the rate of melting were intermediate between the values of sample series 1 and 3. This was to be expected because the thermal treatments of sample series 2 and 4 can be considered intermediate between those of sample series 1 and 3.

It has been shown that the coefficients of thermal expansion did not differ significantly after various thermal treatments. This indicates that there are no differences in coefficients of thermal expansion of mixed and layer crystals. There were differences between the coefficients of thermal expansion of solid and liquid milk fat, the latter was higher than the former.

The melting dilations of milk fat did not differ after various thermal treatments used in this work. The melting dilations of winter milk fat were greater than those of summer milk fat, because of the greater solid fat content of winter milk fat.

The solid fat contents after different thermal treatments varied depending on amount and types of crystals formed during solidification. Rapid cooling of milk fat promoted mixed crystal formation, which caused higher solid fat contents. Mixed crystals contain dissimilar molecules and result in an increase in the solid fat content. Thermal treatments which cause formation of a greater amount of mixed crystals result in a higher solid fat content in milk fat. If slow cooling, or tempering at higher temperatures takes place, the solid fat content decreases.

The presence of mixed crystals causes a high rate of melting of milk fat, whereas the presence of layer crystals promotes a low rate of melting. The reason for the different rates of melting is that layer crystals melt gradually, layer by layer, while the melting of mixed crystals occurs in a narrower temperature range between the lowest and highest melting points of the component glycerides. This is due to a relatively fast disintegration of a mixed crystal as a result of melting of the low melting part of the crystal which links the higher melting fractions together.

It is evident from the results presented that thermal treatment has a definite influence on the melting properties and the solid fat content of milk fat. It is possible to change the physical properties of butter with a suitable thermal treatment during the production. This appears particularly important in the case of continuous butter making. These practical means of influencing the properties of butter can be explained on the basis of the results obtained in this work.

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